PATENT SPECIFICATION

688,637

Date of Application and filing Complete Specification March 23, 1950.

No. 7281/50.

Application made in United States of America on March 23, 1949.

Complete Specification Published March 11, 1953.

Index at acceptance.—**Class 140,** E1(a: h), E2a7.

COMPLETE SPECIFICATION

Improvements in or relating to the Coating of Sheet Material

We, E. I. DU PONT DE NEMOURS AND COMPANY, of Wilmington, Delaware, United States of America, a Company organised and existing under the Laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the coating of sheet materials and, more particularly, to a process of applying a film of a synthetic linear polymer of sharp melting point to a sheet.

Methods have hitherto been described for applying thin coatings of thermoplastic polymers to sheets of paper, cloth, foil, tape and the like. Many of the known methods suffer from one or more disadvantages, or the properties of the resulting coated sheets are defective from the standpoint of commercial utility. For example, it is difficult to apply thin coatings of ethylene polymers and polyamides by hot melt spreading owing to their high melt viscosities and poor stability at melt temperatures; besides, poor adhesion between the coating and the sheet results from this technique. In other cases calendering equipment has been employed to increase the pressure and thereby improve the adhesion between polymer and sheet but this equipment is costly and will not accomplish the desired result in the case of all polymers of the class herein contemplated; for example, polyamides are too readily oxidized at the high temperatures required for calendering. Still another technique to improve the bond between polymer coating and sheet involves the use of adhesives but several inherent disadvantages accrue to these products since the properties of the adhesive are seldom equivalent and usually inferior to those of the polymer selected for a particular application.

British Specification No. 601,713 describes a process for coating sheet materials with ethylene polymers in which a layer of molten polymer is applied to a metal surface, for example, to the surface of a metal drum or continuous metal band, the surface of the material to be coated is pressed against the layer of molten polymer, the polymer is caused or allowed to cool until its surface in contact with the metal surface is solid, and the coated material is removed from the surface.

An object of the present invention is to provide an economical process of applying films of synthetic linear polymers of sharp melting point to sheets. A further object is to provide such a process whereby a strong bond between the film and sheet may be obtained without the use of an intermediate adhesive layer. A more specific object is to provide such a process for applying films of solid ethylene polymers, chlorinated solid ethylene polymers, and polyamides to sheets of paper, cloth or metal foil. Other objects wil lbe apparent from the description of the invention given hereinafter.

These objects are accomplished according to the present invention by a process in which a molten film of a normally solid synthetic linear polymer of sharp melting point is extruded to contact with the sheet to be coated whilst still in a molten condition, the molten film is pressed against said sheet and the surface of the molten film remote from the sheet is chilled to a temperature below the solidification point of the molten film, the contacting and pressing of said molten film against said sheet and its chilling being effected substantially simultaneously.

The process of this invention may be carried through the use of any suitable mechanical means. It is preferred to apply the film of polymer to the sheet by feeding the sheet into the nip of two adjacent parallel rolls rotating in opposite directions (e.g. by extruding a molten film of the polymer parallel to the rolls

and downwardly into the nip of the rolls), the molten film contacting the sheet at the nip of the rolls and not contacting either roll appreciably before the nip, and passing the film and sheet through the nip of the rolls under pressure, the roll in contact with the film being maintained at a temperature below the solidification point of the molten film.

The accompanying drawing illustrates a suitable arrangement of apparatus for carrying out the process of the invention.

In this apparatus, the polymer is extruded by a conventional extrusion machine 1 through the die 2 provided with a narrow slit orifice, to form the molten film 3. A pair of adjacent parallel rolls 4 and 5, rotating in opposite directions as indicated, are positioned below the die 2 so that the molten film 3 travels a short distance substantially vertically to reach the nip 6 of the rolls.

The sheet 7, to which the film 3 is to be applied, is run off the supply roll 8 over and partially around the roll 4 and into the nip 6 of the rolls. The sheet 7 and film 3 contact each other at the nip 6 of the rolls, that is, they are not brought into contact with each other appreciably before that point nor is the film 3 brought into contact with the roll 5 before it reaches the nip 6 of the rolls. Thus, the film 3 and sheet 7 contact each other, are pressed together, and the exposed surface of the film 3 (the other surface being covered by the sheet 7) is chilled by the roll 5, all substantially simultaneously.

The die 2 is arranged so that the distance between it and the nip 6 is extremely short. With such arrangement the temperature of the molten film 3 as it reaches the nip 6 is practically unchanged from its temperature as it left the die 2. The polymer could be heated in the extrusion machine 1 to a temperature considerably above that desired for the film when it reaches the nip 6 and thus permit a greater distance between die 2 and nip 6, since some cooling down of the film would be allowed, or the same result could be obtained by providing means for heating (or preventing cooling) of the film 3 during its travel from die 2 to nip 6, but neither of these alternatives is as practical as simply placing the die 2 close to the nip 6 as illustrated.

The sheet 7 and film 3 continue around the roll 5 to the roll 9, pass over the roll 9 and the coated sheet is then wound up on the storage roll 11.

The roll 4 may if desired be equipped with steam coils or the like for the purpose of heating the sheet 7, and roll 5 is advantageously equipped for cold water circulation to maintain it at a temperature below the solidification point of the film 3. If the roll 4 is not to be heated, there is no need to pass the sheet 7 over and partially around it as the sheet can be fed directly into the nip 6 without previous contact with the roll 4. Nevertheless, the arrangement illustrated is usually convenient regardless of wether the roll 4 is to be heated or not.

Although nothing like the pressure conventionally exerted by calendar rolls is required in the process, wherein lies a substantial advantage, the rolls 4 and 5 should exert some pressure on the sheet and film passing through the nip. This may be conveniently effected by mounting one of the rolls on an eccentric bearing and using a friction drive or other means obvious to those skilled in the art may be used. The pressure can be regulated by the spacing of rolls 4 and 5. Generally, the greater the pressure exerted by these rolls on the sheet and film, the stronger is the bond between the two but there is no necessity for approaching the order of pressure normally used when employing calendaring rolls. At least one of the rolls 4 and 5 should be driven and both may be driven in which latter case they need not necessarily be driven at the same peripheral speed.

The roll 5 should have an incompressible surface; normally a metal roll is used, and the surface may be smooth or, if an embossed effect is desired, its surface may be embossed. The surface of roll 4 may also be of metal or other incompressible material, but it is preferably compressible. A rubber roll is quite suitable.

The thickness of the film can readily be varied through adjusting one or a combination of: the die opening and the screw speed in the extrusion machine, the take-off speed of the united film and sheet, the pressure exerted by the rolls 4 and 5, or the roll 9. The pressure exerted by rolls 4 and 5 at the nip 6 can be regulated by the spacing of these rolls.

The temperature of the molten film at its contact with the sheet may be anywhere from the melting point of the polymer to its decomposition point, but with each polymer there is a preferred temperature range appreciably above its melting point that gives the best operation of the process and the best product with respect to adherence of film to sheet, uniformity of film, and excellence of film surface. In carrying out the preferred process, these particular temperature ranges for films of various polymers form an exceedingly important factor in the

invention where a strong bond between film and sheet is desired. Where such bond is immaterial or actually not desired, for example, where the film is to be stripped from the sheet, a practical procedure if a smooth-surfaced sheet is used, there is no advantage in employing these particular temperature ranges and ordinarily lower temperatures at which the film is molten would be preferred.

The film may be chilled to any temperature below the solidification point of the molten film. The temperature of the sheet at the point of contact with the film is not critical, nor is the pressure used in pressing the sheet and film together, although the adherence of the film to the sheet is improved somewhat as the pressure is increased.

The polymers used in the process of this invention are linear in molecular structure as contrasted with polymers which possess sufficient three-dimensional network of chemical cross-linking to render them insoluble and incapable of being reversibly shaped by heat. These polymers are capable of being cold drawn into fibres which show by X-ray diffraction patterns some degree of microcrystalline structure and orientation along the fibre axis. These polymers have the property of behaving like liquids when melted, i.e., they have relatively sharp melting points and, after passing through a small temperature range wherein they are somewhat plastic, they become relatively free-flowing liquids.

Preferably, the film is formed of a polymer from the group consisting of ethylene polymers, chlorinated ethylene polymers having, preferably, a chlorine content of 20%—40%, and polyamides such as polyhexamethylene adipamide.

With respect to ethylene polymers, the temperature of the molten film as it contacts the sheet may be from 120° C. to 300° C., and is preferably between 220° C. and 260° C., and the film should be chilled to a temperature between 10° C. and 90° C., preferably between 45° C. and 65° C. In the case of chlorinated ethylene polymers, the molten film may be at a temperature of 120° C. to 190° C. and, preferably, between 135° C. and 160° C., at the time of contact with the sheet. The same chilling temperatures as noted above are preferred.

If a polyamide film is used, it may be at a temperature between the melting point of the polyamide and 300° C., preferably not above 275° C. The polyamides divide more or less sharply into those of relatively high melting point and those of relatively low melting point and, with respect to the former, it is preferred to have the film at a temperature of at least 235° C. as it contacts the sheet while a lower minimum temperature of 190° C. is preferred for the latter. The film should be chilled to 10° C. to 120° C. in the case of all the polyamides, with the more limited range of 20° C. to 100° C. being preferred.

Other polymers suitable for use in the process of this invention include polyesters, polyester-amides, polyanhydrides and polyethers. Mixtures of two or more polymers and copolymers may also be used in the film provided they possess the essential characteristics of being normally solid, thermoplastic linear polymers and possess sharp melting points. The polymer film may contain small amounts of conventional modifiers such as softeners, plasticizers, fillers, pigments, dyes, opacifiers, heat- and light-stabilizers, anti-oxidants and lubricants.

The invention is broadly applicable to sheet materials in general. It is particularly useful for the coating of fibrous materials such as paper, wood veneers and woven or knitted fabric sheets formed from fibres composed of such materials as natural or regenerated cellulose, nylon, cellulose derivatives, synthetic resins, asbestos, and glass as well as non-fibrous materials such as regenerated cellulose sheets, metal foil, and thermoplastic films. The thickness of the sheets is not a critical factor since they may range from flexible tissue-like papers to rigid metal sheets although the greatest advantages are realized when the invention is applied to flexible sheets capable of being wound on a roll.

The temperature of the sheet as it contacts the film may vary widely; a temperature of 100° C.—120° C. is slightly preferred as it tends to improve the bond between film and sheet, but there is little preference in the ordinary case for the preheating procedure. It has been observed that while it is necessary to chill the molten film to a temperature below its solidification point, the higher the chilling temperature used, without introducing such difficulties as adhesion of the film to the roll or other means for pressing the sheet and film together, the better is the bond between the sheet and film. Hence the highest feasible chilling temperature which will not cause the resin to adhere to the apparatus is preferably employed.

Our invention is illustrated but in no way limited by the following examples, in which all parts given are by weight.

EXAMPLE I.

Ethylene polymer, having an average molecular weight of 18000—20000 and

containing 0.2% of N,N¹-diphenyl-*p*-phenylene-diamine as an antioxidant, was fed into an extruder having a slit-like die opening 0.005 inch wide. The temperature of the die was kept between 250° C. and 300° C. during the extrusion. The extruded molten film was led through an air gap of 3.25 inches to the nip of two rotating rolls as illustrated in the accompanying drawing. Roll 5 was a cored polished steel roll 3.5 inches in diameter, the surface of which was kept chilled to a temperature of approximately 50° C. by internally circulating cold water. Roll 4 was a rubber roll 2¾ inches in diameter. This roll was at room temperature and was friction driven on an eccentric bearing to allow variation of the pressure. The molten film came into contact with a sheet of paper 0.005 inch thick at the nip of the two rolls. The take-off speed of the united paper and film was varied up to 60 feet per minute and the pressure between the rolls was also varied to give ethylene polymer coatings as thin as 0.0007 inch. An adherent, smooth, even coating of ethylene polymer (0.0007 inch thick) was obtained on the paper at 60 feet per minute take-off speed.

When the surface of roll 5 was allowed to warm up to 90° C. by stopping the circulation of cold water, the polymer film showed some tendency to stick to this roll.

Example II.

The procedure described in Example I was repeated except that chlorinated ethylene polymer (18000 molecular weight ethylene polymer chlorinated to 27% chlorine content) was substituted for the ethylene polymer and the pressure of the rolls was adjusted so that paper sheeting having an adherent film of chlorinated ethylene polymer 0.004 inch thick in one case and 0.008 inch thick in a second run, was obtained. The only difference in the operating conditions from Example I was that the temperature of the extrusion die was 160° C.—165° C. The process operated as smoothly as in Example I and the resulting product was equally satisfactory.

Example III.

The process described in Example I was repeated except that roll 4 delivered simultaneously a 0.0005 inch thick aluminum foil backed with 0.005 inch Kraft paper. Since the metal foil was too weak to be processed as in Example I, the paper was fed to roll 4 as a physical backing to strengthen and support the metal foil during the process. The same temperature conditions were used as in Example I and a take-off speed of 60 feet per minute was achieved in producing a 0.0015 inch coating of ethylene polymer on the metal foil. The paper was readily stripped off the back of the foil, leaving a flexible ethylene polymer coated aluminum foil useful as a moisture-proof packaging material.

Example IV.

A polyamide obtained by interpolymerizing a mixture of 40 parts of hexamethylene-diammonium adipate, 30 parts of hexamethylene-diammonium sebacate and 30 parts of caprolactam was extruded into a film and applied to a 0.003 inch cloth using the equipment as in Example I, except that rolls 4 and 5 were both of polished steel. The temperature of the die on the extrusion machine was held at 240° C. to 250° C. while the temperature of both rolls 4 and 5 was 100° C. The die opening and take-off speed were adjusted to give a 0.012 inch film of polyamide on the cloth and the two rolls were placed close enough together to exert positive pressure on the film and the cloth sheet as it passed through the nip of the rolls, with the result that adherence between the two was good. The polyamide film was highly polished, smooth and continuous, and could be stripped from the cloth only with difficulty.

The polished steel roll 5 used in this Example was replaced by an embossed steel roll and the apparatus run again under identical conditions with the result that an embossed polyamide coating was obtained.

Example V.

The procedure described in Example I was repeated except that the roll 4 was equipped with internal coils for circulating steam and the temperature of the roll was kept at 104° C.—110° C. The paper sheet was thus preheated to about the same temperature as the roll by the time it contacted the polymer film. The resulting coated product was similar to that obtained in Example I but the bond between the ethylene polymer film and paper sheet was even stronger.

An advantage of this invention is that it provides a rapid process for the coating of sheets with thermoplastic polymers incapable of being handled by the conventional calendering process because of their sharp high melting point and property of being easily oxidised at the temperature of calendering. Another advantage is that the process requires only light weight, low cost equipment because the pressures necessary for coating and bonding are low due to the molten condition of the polymer, and the method of effecting temperature control may be very simple. This process is particularly advantageous

for the application of thin coatings, especially those less than 0.010 inch, coatings down to 0.0005 inch thick having been applied with satisfactory results. Also of advantage in the application of thin coatings is the fact that this process lends itself readily to the filtering of the molten polymer continuously prior to the application of the molten film to the sheet. This insures removal of foreign particles and polymer agglomerates which frequently interfere with the production of smooth coatings of uniform thickness free from surface imperfections.

The coated sheets obtained by the process of this invention, especially when prepared under the preferred conditions leading to maximum adhesion between the sheet and polymer film, are useful in various wrapping and packaging applications as substitutes for metal foils, regenerated cellulose or like film, wax paper and the like. However, the invention may also be used for coating non-fibrous sheets such as regenerated cellulose or like film and aluminum foil under conditions which do not lead to a strong bond between the sheet and film. Such coated sheets are put to use by stripping the polymer film from the smooth surface of the sheet and in this way there are obtained thin, transparent, self-supporting films useful in the packaging industry. Such polymer film possesses maximum strength, clarity, transparency, smoothness and uniformity of thickness and is free from surface irregularities such as pits, air bubbles, streaks, undulations and crazing such as may result from solvent casting.

The coated sheets produced according to the process of this invention are useful in a wide variety of commercial and household applications. Among such uses are packaging for foods including storage of frozen foods, cigarette packaging, packaging of cosmetics and other perishable materials, flexible waterproof map backings and/or transparent protective coatings for map faces, insulating tapes, cartons and containers, closure liners, tank linings, multi-wall paper bags, adhesive tape backings, electrical insulation, wearing apparel such as raincoats, shower curtains, box toes and counters for shoes, artificial leather, floor and wall coverings, window shades, book bindings and the like. These are examples of using the coated sheets as they are fabricated to make use of the properties of moisture resistance, low moisture penetration, and low electrical conductivity and power factor which are especially noticeable in the ethylene polymer coated sheets. Other uses for the coated sheets include that of using the polymer coatings for masking purposes such as applying a transparent polymer film (e.g. ethylene polymer) to the printed surface of wall paper to produce a washable wall paper which may be changed by first stripping the polymer coating; and that of using the coated sheets for transfer coating from the backing sheet to another sheet material by suitable well known means, such as hot pressing. A further useful application of this invention is in the production of laminates, such as by feeding a previously prepared ethylene polymer coated paper to roll 4, with the polymer coating next to the surface of the roll, and running the process as before. This results in an ethylene polymer/paper/polymer laminate which is useful for a variety of purposes such as packaging various articles. The second coating of polymer may be the same as the first (e.g. ethylene polymer in this instance) or it may be any other desired thermoplastic polymer.

What we claim is:—

1. A process for the production of coatings on sheets wherein a molten film of a normally solid synthetic linear polymer of sharp melting point is extruded to contact with the sheet to be coated whilst still in a molten condition, the molten film is pressed against said sheet and the surface of the molten film remote from the sheet is chilled to a temperature below the solidification point of the molten film, the contacting and pressing of said molten film against said sheet and its chilling being effected substantially simultaneously.

2. A process according to claim 1 in which said sheet is fed into the nip of two adjacent parallel rolls rotating in opposite directions, a molten film of said synthetic linear polymer is fed downwardly into the nip of the rolls without contacting either roll appreciably before the nip, and the molten film and sheet are passed through the nip under pressure, the roll in contact with the film being maintained at a temperature below the solidification point of the molten film.

3. A process according to either of the preceding claims in which said polymer is a polymer of ethylene.

4. A process according to claim 3 in which the temperature of the molten film when it contacts the sheet is 120° C. to 300° C.

5. A process according to claim 4 in which the temperature of the molten film when it contacts the sheet is 220° C. to 260° C.

6. A process according to claim 1 or claim 2 in which said polymer is a

chlorinated polymer of ethylene, having a chlorine content of 20% to 40% by weight.

7. A process according to claim 6 in which the temperature of the molten film when it contacts the sheet is 120° C. to 190° C.

8. A process according to claim 7 in which the temperature of the molten film when it contacts the sheet is 135° C. to 160° C.

9. A process according to any of the preceding claims in which the molten film is chilled to a temperature between 10° C. and 90° C.

10. A process according to claim 9 in which the molten film is chilled to a temperature between 45° C. and 65° C.

11. A process according to claim 1 or claim 2, in which said polymer is a polyamide.

12. A process according to claim 11 in which the temperature of the molten film when it contacts the sheet is below 300° C.

13. A process according to claim 12 in which the temperature of the molten film when it contacts the sheet is not above 275° C.

14. A process according to any of claims 11 to 13 in which the molten film is chilled to a temperature of 10° C. to 120° C.

15. A process according to claim 14 in which the molten film is chilled to a temperature of 20° C. to 100° C.

16. A process according to any of the preceding claims in which the temperature of the sheet as it contacts the molten film is 100° C. to 120° C.

17. A process for the coating of sheets substantially as hereinbefore described with particular reference to any of the foregoing Examples or to the accompanying drawing.

18. Coatings on sheet materials whenever produced by a process according to any of the preceding claims.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1953.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

688,637 COMPLETE SPECIFICATION
1 SHEET

This drawing is a reproduction of the Original on a reduced scale.